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(54) High styrene content stable polymer polyols using epoxy resin-modified polyols as base polyols.

(57) Low viscosity polymer polyols having styrene/acrylonitrile ratios, which may be as high as 95/5 or even 100/0, and good stability are obtained by polymerising a monomer component having a styrene portion and an acrylonitrile portion in the presence of an epoxy resin-modified polyol as the base polyol. The epoxy resin-modified polyols useful as base polyols are preferably made by reacting a polyol initiator having an active hydrogen functionality of 3 to 8 and one or more alkylene oxides with an epoxy resin. Preferably, only a small part of the epoxy resin-modified base polyol is initially charged to the reactor, and the balance forms a part of the monomer feed stream to the reactor.

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**HIGH STYRENE CONTENT STABLE POLYMER POLYOLS USING EPOXY RESIN-MODIFIED POLYOLS AS
BASE POLYOLS**

The invention relates to the synthesis of polymer polyols, and, in one aspect, more particularly relates to styrene/acrylonitrile (SAN) copolymer polyols with high styrene contents employing epoxy resin-modified polyols as the base polyols. This application is related to European patent application No. 89 (Case No. 15 179), filed of even date with this application.

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Background of the Invention

10 The use of a polyol in the preparation of polyurethanes by reaction of the polyol with a polyisocyanate in the presence of a catalyst and perhaps other ingredients is well known. Conventional polyols for flexible polyurethane foams, such as slab urethane foams, are usually made by the reaction of a polyhydric alcohol with an alkylene oxide, usually ethylene oxide and/or propylene oxide, to a molecular weight of about 2,000 to 5,000 and above. These polyols are then reacted with polyisocyanate in the presence of water or other
15 blowing agents such as fluorocarbons to obtain polyurethane foams. Polyols have been modified in many ways in attempts to improve the properties of the resulting polyurethane; for example, by using a polymer polyol as the polyol component. Conventional polyols may be used as the dispersing media or base polyol in these polymer polyols.

For example, dispersions of polymers of vinyl compounds such as styrene, acrylonitrile or a mixture of
20 the two (abbreviated as SAN monomers), or of polyurea polymers, such as those prepared from toluene diisocyanate (TDI) and hydrazine in conventional polyols have been included to improve the properties of the polyols, and thus, the properties of the resulting foam. Polyurethane foams with higher load bearing properties (ILD - indentation load deflection, and CFD -compression force deflection) may be produced in this manner. It would be desirable if polymer polyols could be prepared which would be stable and have
25 low viscosities. Stability is important to the storage life of the polyols before they are used to make the polyurethane foams. Low viscosities and small particle sizes are important in a good quality polyol to permit it to be pumped easily in high volume foam producing equipment.

It would further be desirable if styrene/acrylonitrile polymer polyols could be synthesized which would have large SAN ratios. The substitution of styrene for acrylonitrile in these polymer polyols helps prevent
30 discoloration during the cure of the polyurethane, and also helps to improve flame retardability of the resultant foams. However, the stability of the polymer polyols decreases with increasing styrene to acrylonitrile ratios. That is, the components tend to separate upon standing during storage. Viscosity and particle size are also typically adversely affected with high styrene contents.

U.S. Pat. Nos. 4,539,378 and 4,539,339 describe polymer polyols made using epoxy resin-modified
35 polyols and polyurethane foams prepared therefrom. The improvement claimed in these patents is that polymer polyols made using these epoxy resin-modified polyols as base polyols give flexible polyurethane foams with greater load bearing properties than if made with other polyols. The use of the base epoxy resin-modified polyol in polyurethane foams to give foams with enhanced properties was known at this time by virtue of U.S. Pat. No. 4,316,991. Although it is claimed therein that the monomer component is a
40 mixture of styrene and acrylonitrile in a mole ratio of 9:1 to 1:9, equivalent to a weight ratio of about 18:1 to 1:18, all examples given therein are at styrene/acrylonitrile ratios of 40/60. In prefacing the examples therein with a general conditions statement, it is asserted that to obtain the vinyl polymer polyols of the invention, all of the epoxy resin modified polyol is preferably added first to the reaction vessel. This teaching is consistent with the examples therein.

45 It is well known in the art that high styrene content polymer polyols are desirable, but difficult to prepare for the reasons stated above. Regardless of the teachings of the patents discussed above, it would be unexpected to find that epoxy resin-modified polyols may be useful in preparing polymer polyols that did not only have high styrene contents, but which also had good stability, small particle sizes, and low viscosity.

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Summary of the Invention

Accordingly, it is an object of the present invention to provide stable, low viscosity polymer polyols at high styrene to acrylonitrile (SAN) ratios, and a method for making such polymer polyols. In one aspect of the invention, these SAN ratios may range from about 65/35 to even 100/0.

It is another object of the present invention to provide a particular process for the production of the stable, low viscosity SAN polymer polyols of the present invention using epoxy resin-modified polyols as the base polyol.

It is yet another object of the invention to provide stable, low viscosity polymer polyols of high SAN ratios employing epoxy resin-modified polyols as the base polyol with no dispersant. In one aspect of the invention the epoxy resin-modified polyols are added in two portions, one with the reactor charge and the other in the reactor feed stream.

In carrying out these and other objects of the invention, there is provided, in one form, stable, low viscosity polymer polyols made by a process of polymerizing, via a free-radical reaction, a monomer component having a styrene portion and an acrylonitrile portion, in the presence of an epoxy resin-modified polyol as the base polyol, where the wt. ratio of the styrene portion to the acrylonitrile portion ranges from greater than 60/40 to 100/0.

Detailed Description of the Invention

It has been surprisingly discovered that a process using epoxy resin-modified polyols as the base polyol can produce improved polymer polyols with low viscosity, good stability and very high SAN weight ratios with no dispersants. A smaller average particle size of the dispersed solid is also obtained. The method produces stable, low viscosity polymer polyols at SAN ratios of from about 65/35 to even 100/0. The reactor may be a batch reactor, a semi-batch reactor or one or more continuous stirred tank reactors (CSTRs).

In one aspect of the invention, the epoxy resin-modified base polyol is added in two portions. The first portion is added with the charge to the reactor, and the second portion is added in the feed stream to the reactor. In another embodiment, the first portion is less than the second portion. When two portions of epoxy resin-modified polyols are used as base polyol, the ratio of the first portion of base polyol to second portion thereof may range from 1/99 to 50/50, preferably from 5/95 to 30/70, based on weight.

Without dispersants or other special techniques, typical conventional SAN ratios could only reach as high as the range of about 60/40-65/35. In contrast, the SAN ratios that can be supported by the polymer polyols of the present invention range from 65/35-100/0, more commonly being in the range of about 75/25-95/5.

The base polyols may be polyols known to have been modified with epoxy resins. For example, U.S. Pat. No. 4,495,341 to Stamberger describes adducts produced by reacting suitable polyol and epoxy co-reactants to essentially eliminate all epoxy groups. In one embodiment therein, the amount of epoxy co-reactant is greater than 2% but less than 10% by weight based on the amount of polyol. In a preferred embodiment of the present invention, however, the base polyol is made by the method described in U.S. Pat. No. 4,316,991 to Speranza, incorporated by reference herein. Briefly, these epoxy resin-modified polyols may be made by reacting a polyol initiator with one or more alkylene oxides to extend the polyol chain, and adding epoxy resin. Although U.S. Pat. No. 4,316,991 indicates that the epoxy resin is added at selected points internally along the length of the polyol chain, it is anticipated herein that epoxy resin-modified polyols made using the epoxy resin as a cap, or both as a cap and internally, would give modified polyols suitable in synthesizing the polymer polyols of the present invention.

In one aspect of the invention, it is recommended that in the preparation of the epoxy resin-modified base polyols, at least two equivalents of hydroxyl functionality be present per equivalent of epoxy resin added to the reaction mixture to avoid gelling of the epoxy by crosslinking with itself. The epoxy resin may be added before, during and/or after the addition of alkylene oxide to the polyol initiator. In one aspect of the invention, good results are obtained if the resin is not added only as a "cap", that is, after all of the oxide has been added which results in the resin being attached to the end of the resulting polyol chain only. The wt.% of epoxy resin added based on the final base polyol may range from about 0.25 to about 5.0 wt.% or higher in a broadest range, and from about 0.25 to 2.0 wt.% in a somewhat narrower range. The preferred range of epoxy resin proportion is from about 0.5 to about 1.5 wt.%. One skilled in the art may determine the best procedure with respect to when additions should be made and at what temperature and during which times the reaction mixture is to be heated.

It is well known that polyethers for polyurethane applications can be prepared by the base catalyzed

reaction of an alkylene oxide with an initiator having a low hydrogen functionality, that is, containing from three to four reactive hydrogen atoms. Such initiators include, for example, glycerine, trimethylolpropane (TMP), 1,2,6-h xanetriol, pentaerythritol, alkanolamines such as triethanolamine, alkylamines such as ethylenediamine, aryl or aromatic amines such as aminoethylpiperazine, sorbitol, α -methylglucoside, β -methylglucoside or other methylglucoside, resins of phenol, aniline and mixed phenol aniline, such as methylenedianiline or bisphenol A, Mannich condensates and mixtures thereof. If base catalysis is used, the alkaline catalysts normally employed are sodium hydroxide and potassium hydroxide. Other techniques to prepare polyols are well known in the art. One or more alkylene oxides may be added together or in series to the polyhydric or polyfunctional initiators using well known techniques to make mixed or block copolymers.

The alkylene oxides useful in this invention are ethylene oxide, propylene oxide, 1,2-butylene oxide and mixtures thereof. Ethylene oxide and propylene oxide are preferred for this invention. More than one alkylene oxide may be added to the reaction mixture as deemed necessary by one skilled in the art.

It is anticipated that a wide variety of epoxy resins would be useful in making the epoxy resin-modified base polyols useful herein. The vicinal polyepoxide containing compositions are organic materials having an average of at least 1.8 reactive 1,2-epoxy groups per molecule. These polyepoxide materials can be monomeric or polymeric, saturated or unsaturated, aliphatic, cycloaliphatic, aromatic or heterocyclic, and may be substituted if desired with other substituents besides the epoxy groups, e.g. hydroxyl groups, ether radicals, aromatic halogen atoms and the like.

Preferred polyepoxides are those of glycidyl ethers prepared by epoxidizing the corresponding allyl ethers or reacting, by known procedures, a molar excess of epichlorohydrin and an aromatic polyhydroxy compound, i.e. isopropylidene bisphenol, novolak, resorcinol, etc. The epoxy derivatives of methylene or isopropylidene bisphenols are especially preferred. The diglycidyl ether of bisphenol A is particularly useful. Some of these epoxy resins are known in the trade as "Epon" resins and may be obtained from Shell Chemical Co.

A widely used class of polyepoxides which are useful includes the resinous epoxy polyethers obtained by reacting an epihalohydrin, such as epichlorohydrin, and the like, with either a polyhydric phenol or a polyhydric alcohol. An illustrative, but by no means exhaustive, listing of suitable dihydric phenols includes 4,4'-isopropylidene bisphenol, 2,4'-dihydroxydiphenylethylmethane, 3,3'-dihydroxydiphenyldiethylmethane, 3,4'-dihydroxydiphenylmethylpropylmethane, 2,3'-dihydroxydiphenylethylphenylmethane, 4,4'-dihydroxydiphenylpropylphenylmethane, 4,4'-dihydroxydiphenylbutylphenylmethane, 2,2'-dihydroxydiphenylditolylmethane, 4,4'-dihydroxydiphenyltolylmethylmethane and the like. Other polyhydric phenols which may also be co-reacted with an epihalohydrin to provide these epoxy polyethers are such compounds as resorcinol, hydroquinone, substituted hydroquinones, e.g., methylhydroquinone, and the like.

Among the polyhydric alcohols which can be coreacted with an epihalohydrin to provide these resinous epoxy polyethers are such compounds as ethylene glycol, propylene glycols, butylene glycols, pentane diols, bis(4-hydroxycyclohexyl)dimethylmethane, 1,4-dimethylolbenzene, glycerol, 1,2,6-hexanetriol, trimethylolpropane, mannitol, sorbitol, erythritol, pentaerythritol, their dimers, trimers and other polymers, e.g., polyethylene glycols, polypropylene glycols, triglycerol, dipentaerythritol and the like, polyallyl alcohol, polyhydric thioethers, such as 2,2'-3,3'-tetrahydroxydipropylsulfide and the like, mercapto alcohols such as monothioglycerol, dithioglycerol, and the like, polyhydric alcohol partial esters, such as monostearin, pentaerythritol monoacetate, and the like, and halogenated polyhydric alcohols, such as monochlorohydrins of glycerol, sorbitol, pentaerythritol and the like.

Another class of polymeric polyepoxides which can be amine cured and are useful includes the epoxy novolak resins obtained by reacting, preferably in the presence of a basic catalyst, e.g., sodium or potassium hydroxide, an epihalohydrin, such as epichlorohydrin, with the resinous condensate of an aldehyde, e.g., formaldehyde, and either a monohydric phenol, e.g., phenol itself, or a polyhydric phenol. Further details concerning the nature and preparation of these epoxy novolak resins can be obtained in H. Lee, et al. *Handbook of Epoxy Resins*, McGraw Hill Book Co., New York, 1967.

It will be appreciated by those skilled in the art that the polyepoxide compositions which are useful according to the procedure of making the epoxy resin-modified polyols useful in the present invention are not limited to those containing the above described polyepoxides, but that these polyepoxides are to be considered merely as being representative of the class of polyepoxides as a whole.

The reaction conditions of temperature and pressure may be selected by the invention practitioner to meet certain specifications required by the polyol for making SAN polymer polyols. A pressure of about 50 psig and a temperature of from about 50 to 150 °C. are representative conditions for the making of the epoxy resin-modified polyols. The amount of epoxy resin to be added to the reaction mixture should be such that the epoxy equivalents present are less than half of the hydroxyl functionality equivalents present

in the reaction mixture. Too many epoxy equivalents in relation to the hydroxyl equivalents may cause the epoxy resin to gel by cross-linking with itself. As a result, a large excess of hydroxyl equivalents may be used in the reaction mixture. The modified polyol resulting from this method would preferably have a molecular weight in the range of 2,000 to 7,000. It is conceivable that higher molecular weight modified polyols could be prepared by the methods of this invention.

The preparation of the polymer polyols of the present invention may be performed at a temperature in the range of 80 to 150 °C., preferably in the range of about 100 to 130 °C.

Any suitable addition time of the feed stream to the reactor contents may be employed, for example, the addition time may range from 0.5 to 4.0 hours, preferably 1 to 2.5 hours. The proportion of the polymerization initiator as a wt.% of the total reactants may range from 0.05 to 5.0 wt.%, preferably 0.1 to 1.0 wt.%.

The preferred monomers employed in the method and polymer polyols of the present invention are both styrene and acrylonitrile to make a copolymer. The relative proportions of styrene to acrylonitrile, the SAN ratio, has been discussed above and will exemplified below. Other suitable monomers include, but are not limited to, butadiene, isoprene, 1,4-pentadiene, 1,6-hexadiene, 1,7-octadiene, styrene, acrylonitrile, methacrylonitrile, α -methylstyrene, methylstyrene, 2,4-dimethylstyrene, ethyl styrene, isopropylstyrene, butylstyrene, substituted styrenes, such as cyanostyrene, phenylstyrene, cyclohexylstyrene, benzylstyrene, substituted styrenes such as cyanostyrene, nitrostyrene, N,N-dimethylaminostyrene, acetoxystyrene, methyl 4-vinylbenzoate, phenoxystyrene, p-vinyl diphenyl sulphide, p-vinylphenol oxide, acrylic and substituted acrylic monomers such as acrylic acid, methacrylic acid, methyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, methyl methacrylate, cyclohexyl methacrylate, benzyl methacrylate, isopropyl methacrylate, octyl methacrylate, ethyl α -ethoxyacrylate, methyl α -acetoaminoacrylate, butyl acrylate, 2-ethylhexyl acrylate, phenyl acrylate, phenyl methacrylate, N,N-dimethylacrylamide, N,N-dibenzylacrylamide, N-butylacrylamide, methacrylyl formamide, vinyl esters, vinyl ethers, vinyl ketones, vinyl acetate, vinyl alcohol, vinyl butyrate, isopropenylacetate, vinyl formate, vinyl acrylate, vinyl methacrylate, vinyl methoxy acetate, vinyl benzoate, vinyl toluene, vinyl naphthalene, vinyl methyl ether, vinyl ethyl ether, vinyl propyl ethers, vinyl butyl ethers, vinyl 2-ethylhexyl ether, vinyl phenyl ether, vinyl 2-methoxyethyl ether, methoxybutadiene, vinyl 2-butoxyethyl ether, 3,4-dihydro-1,2-pyran, 2-butoxy-2-vinyloxy diethyl ether, vinyl 2-ethylmercaptoethyl ether, vinyl methyl ketone, vinyl ethyl ketone, vinyl phenyl ketone, vinyl ethyl sulfide, vinyl ethyl sulfone, N-methyl-N-vinyl acetamide, N-vinylpyrrolidone, vinyl imidazole, divinyl sulfide, divinyl sulfoxide, divinyl sulfone, sodium vinyl sulfonate, methyl vinyl sulfonate, N-vinyl pyrrole, dimethyl fumarate, dimethyl maleate, maleic acid, crotonic acid, fumaric acid, itaconic acid, monomethyl itaconate, t-butylaminoethyl methacrylate, dimethylaminoethyl methacrylate, glycidyl acrylate, allyl alcohol, glycol monoesters of itaconic acid, vinyl pyridine, maleic anhydride, maleimide, N-substituted maleimides, such as N-phenylmaleimide and the like.

The polymerization initiator catalyst may be any suitable initiator for the particular monomers employed. Suitable catalytic initiators useful in producing the polymer polyol compositions of this invention are the free radical type of vinyl polymerization catalysts, such as the peroxides, persulfates, perborates, percarbonates, azo compounds, and the like. Specific examples include, but are not limited to, 2,2'-azo-bis-isobutyronitrile (AIBN), dibenzoyl peroxide, lauroyl peroxide, di-t-butyl peroxide, diisopropyl peroxide carbonate, t-butyl peroxy-2-ethylhexanoate, t-butylperpivalate, 2,5-dimethyl-hexane-2,5-di-per-2-ethyl hexoate, t-butylper-neodecanoate, t-butylperbenzoate, t-butyl percrotonate, t-butyl perisobutyrate, di-t-butyl perphthalate, 2,2'-azo-bis(2-methylbutanenitrile) for example. Other suitable catalysts may be employed, of course.

Procedures for Measurements of Physical Properties of Polymer Polyols

Viscosity was measured using a Brookfield cone and plate viscometer, Spindle #CP-52, operated at 20 secs⁻¹ at 25 °C.

Particle sizes were measured using a Coulter N4 Particle Size Analyzer with o-xylene or isopropyl alcohol as the dispersing media.

Centrifugable solids were determined by centrifuging a sample of the polymer polyol for about 24 hours at about 3300 rpm and 1470 radial centrifugal "g" forces. The centrifuge tube was then inverted and allowed to drain for 4 hours. The non-flowing cake at the bottom of the tube is reported as weight percent of the initial weight of the sample tested.

The method and polymer polyols of the invention will be further described with respect to the following illustrative examples.

EXAMPLES 1-7

All the polymer polyols prepared according to the method of the invention incorporated some version of the following experimental procedure unless otherwise specified. Into a 3 liter, 4-neck resin kettle equipped with stirrer, condenser, thermometer, addition tube, were charged the indicated amounts of base polyol under a blanket of nitrogen. After heating the reactor charge to reaction temperature, the feed charge or stream was added over the indicated time period to give a milk-white polymer polyol. Upon completion of the addition, the polymer polyol was held at the indicated reaction temperature for from 0.5 to 1.0 hours, the soak time or digest time, and then the reaction mixture was stripped for 1.5 to 2.5 hours at about 90 to 120° C. at less than 5 mmHg to yield the polymer polyols.

For examples 1-7, the initiator was Vazo 67, and the digestion time was 0.5 hours. No dispersant was used in any of these examples.

Example 1 was made using THANOL® 5505 (4800 MW, OH# 34) as the base polyol. This polyol has not been modified with an epoxy resin and gives an unsuitable polymer polyol at a SAN ratio of 75/25. The viscosity was 8000, the particle sizes were greater than 3 μ m and the wt.% centrifugable solids were 9.4. Note additionally that Example 7 employs THANOL 5505 where the SAN ratio was 85/15; no polymer polyol was formed - a two phase system resulted. By way of contrast, Examples 2-6 were made using THANOL® 5507 (4700 MW, OH#34) that is similar to THANOL 5505 except that it has been modified with the diglycidyl ether of bisphenol A in accordance with the procedures described above. In all examples, even Example 6 which has an unusually high SAN ratio of 90/10, the viscosities, the particle sizes and the centrifugable solids are all desirably low. Note also that a comparison of Examples 2,3 and 4 indicate that the resulting polymer polyols have lower viscosities if progressively less of the epoxy resin-modified polyol is added as the reactor charge in a first portion than is added subsequently in the feed stream.

TABLE I

Example No.	1	2	3	4	5	6	7
Monomer Charge, Wt. %	20	20	20	20	20	20	20
SAN Weight Ratio	75/25	75/25	75/25	75/25	75/25	90/10	85/15
% of Total Polyol in Feed	70	0	70	90	70	90	89
Reaction Temp., ° C.	120	120	120	120	120	120	120
Initiator Conc., Wt. %	0.5	0.25	0.25	0.25	0.25	0.25	0.5
Feed, Addition Time, hr.	2	1.7	2	1.8	1	2	2
Reactor Charge, g.							
Base Polyol	480	1600	480	160	480	160	176
Feed, g.							
Styrene	300	300	300	300	300	360	300
Acrylonitrile	100	100	100	100	100	40	100
VAZO 67	10	5	5	5	5	5	10
Base Polyol	1120	-	1120	1440	1120	1440	1424
Toluene	10	-	-	-	-	-	10
Polymer Polyol Properties							
Overall Monomer Conv., %	96	93.4	94.0	94.3	93.9	92.5	*
Viscosity cps, 20/sec	8000	3510	3145	2876	2760	2320	
Particle Size, μ	>3	0.60	0.86	1.00	0.74	1.39	
Centrifugable Solids, Wt. %	9.4	3.0	2.4	2.4	2.0	5.6	

*No polymer polyol was formed, a two phase system occurred.

EXAMPLES 8-13

Table 2 illustrates additional examples of the invention at even increased SAN ratios of 95/5 and 100/0. Different base polyols were also employed. Note that the viscosity, average particle size, and centrifugable solids % all remain acceptable in most cases. Conditions were the same as for examples 1-6.

TABLE II

Example No.	8	9	10	11	12	13
Monomer Charge, Wt. %	20	20	20	25	30	20
SAN Weight Ratio	95/5	100/0	100/0	75/25	75/25	75/25
Base Polyol	1	1	2	1	1	3
% Dispersant of Total Polyol	0	0	0	0	0	0
% of Total Polyol in Feed	90	90	90	90	90	90
Reaction Temp., °C.	120	120	120	120	120	120
Initiator Conc., Wt. %	0.25	0.35	0.5	0.31	0.38	0.5
Feed, Addition Time, hr.	2	2	2	1.8	1.8	2.0
Reactor Charge, g.						
Base Polyol	160	160	160	150	140	160
Feed, g.						
Styrene	380	400	400	375	450	300
Acrylonitrile	20	0	0	125	150	100
VAZO 67	5	7	10	6.1	7.5	10.0
Base Polyol	1440	1440	1440	1350	1260	1440
Polymer polyol Properties						
Overall Monomer Conv., %	89.5	88.9	91.6	95.4	96.8	89
Viscosity cps, 20/sec	2100	2090	2580	3600	5100	1480
Particle Size, μ	1.65	>3	>3	1.08	1.20	1.52
Centrifugable Solids, Wt. %	14.9	18.1	2.8	3	4.8	6.8
Polyols:						

¹ Thanol® SF-5507

² 0.67% Epoxy modified ARCOL® 1372

³ Thanol F-3550

PREPARATION OF POLYURETHANE FOAMS

It has been found that molded polyurethane foams may be made by reacting the vinyl (SAN) polymer polyols described above with an organic polyisocyanate in the presence of a polyurethane formation catalyst. In one aspect, the polymer polyol useful in molded foam employs a polyol modified with about 102 wt. % epoxy resin based on the total polyol. A blowing agent such as halocarbon (e.g. trichlorofluoromethane), water or carbon dioxide may also be present. The polyurethane formation catalysts are typically tin catalysts or tertiary amine compounds. Other additives, such as silicone surfactants, etc. may also be present. For more information on preparing polyurethanes, particularly flexible polyurethanes, see U.S. Pat. Nos. 4,338,408; 4,342,687 and 4,381,353, incorporated by reference herein. It is noted that the foams made using the SAN polymer polyols described herein have good load bearing properties. Flexible carpet underlay foam and molded automobile foam with lower polymer loadings and better load bearing properties may be prepared using the techniques mentioned herein. These improvements could be accomplished with lower levels of polymer polyol, which is a significant advantage in foam manufacture.

The polymer polyols prepared in accordance with the above examples may also be incorporated into a formulation which results in a slab polyurethane product. The polymer polyol of the invention may be used in conjunction with a polyisocyanate or may be combined with additional polyols well known in the art, and reacted with a polyisocyanate to form a slab polyurethane foam product. In one aspect of the invention, the

polymer polyol of this invention for a slab polyurethane foams employs polyols modified with about 1-2 wt.% epoxy resin.

In order to form the slab polyurethane foam, a catalyst useful in preparing foams of this type is employed in the usual manner. Such catalyst may include those mentioned above, or one or more of the following:

(a) Tertiary amines such as trimethylamine, triethylamine, N-methylmorpholine, N-ethylmorpholine, N,N-dimethylbenzylamine, N,N-diethylethanolamine, N,N,N',N'-tetramethyl-1,3-butanediamine, N,N-dimethylpiperazine, 1,4-diazobicyclo[2.2.2]octane and the like;

(b) Tertiary phosphines such as trialkylphosphines, dialkylbenzylphosphines, and the like;

(c) Strong bases such as alkali and alkaline earth metal hydroxides, alkoxides, and phenoxides;

(d) Acidic metal salts of strong acids such as ferric chloride, stannic chloride, stannous chloride, antimony trichloride, bismuth nitrate and chloride, and the like;

(e) Chelates of various metals such as those which can be obtained from acetylacetone, benzoylacetone, trifluoroacetyl acetone, ethyl acetoacetate, salicylaldehyde, cyclopentanone-1-carboxylate, acetylacetoneimine, bisacetylacetonealkylenediamines, salicylaldehydeimine, and the like, with various metals such as Be, Mg, Zn, Cd, Pd, Ti, Zr, Sn, As, Bi, Cr, Mo, Mn, Fe, Co, and Ni;

(f) Alcoholates and phenolates of various metals such as $Ti(OR)_4$, $Sn(OR)_4$, $Al(OR)_3$, and the like, wherein R is alkyl or aryl, and the reaction products of alcoholates with carboxylic acids, beta-diketones, and 2-(N,N-dialkylamino)alkanols;

(g) Salts of organic acids with a variety of metals such as alkali metals, alkaline earth metals, Al, Sn, Pb, Mn, Co, Ni, and Cu, including, for example, sodium acetate, stannous octoate, stannous oleate, lead octoate, metallic driers such as manganese and cobalt naphthenate, and the like; and

(h) Organometallic derivatives of tetravalent tin, trivalent and pentavalent As, Sb, and Bi and metal carbonyls of iron and cobalt.

Of course, combinations of any of the above polyurethane catalysts may be employed. Usually, the amount of catalyst employed ranges from about 0.01 to about 5.0 parts by weight percent based on 100 parts by weight of the polyol. More often the amount of catalyst used is 0.2 to 2.0 parts by weight.

As is well known, the polyol component for the polyurethane foam is reacted in the presence of one or more of the above catalysts with a polyisocyanate according to conventional procedures. The polyisocyanate used may be any aromatic or aliphatic polyisocyanate, such as toluene diisocyanates, polymeric isocyanates and aliphatic diisocyanates. Typical aromatic polyisocyanates include, but are not limited to, m-phenylene diisocyanate, p-phenylene diisocyanate, polymethylene polyphenylisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, dianisidine diisocyanate, bitolylene diisocyanate, naphthalene-1,4-diisocyanate, diphenylene-4,4'-diisocyanate, aliphatic-aromatic diisocyanates, such as xylylene-1,4-diisocyanate, xylylene-1,2-diisocyanate, xylylene-1,3-diisocyanate, bis(4-isocyanatophenyl)methane, bis(3-methyl-4-isocyanatophenyl)methane, and 4,4'-diphenylpropane diisocyanate. Suitable aliphatic diisocyanates would include isophorone diisocyanate, hexamethylene diisocyanate and methylene-bis-cyclohexylisocyanate. Toluene diisocyanates are preferred.

Aromatic polyisocyanates suitable for use include methylene-bridged polyphenyl polyisocyanate mixtures which have a functionality of from about 2 to about 4. These latter isocyanate compounds are generally produced by the phosgenation of corresponding methylene bridged polyphenyl polyamines, which are conventionally produced by the reaction of formaldehyde and primary aromatic amines, such as aniline, in the presence of hydrochloric acid and/or other acidic catalysts. Known processes for preparing the methylene-bridged polyphenyl polyisocyanates and corresponding methylene-bridged polyphenyl polyisocyanates therefrom are described in the literature and in many patents; for example, U.S. Pat. Nos. 2,683,730; 2,950,263; 3,012,008; 3,344,162; and 3,362,979.

Often, the most preferred methylene-bridged polyphenyl polyisocyanate mixtures used here contain from about 20 to about 100 wt.% methylene diphenyl diisocyanate isomers with the remainder being polymethylene polyphenyl diisocyanates having higher functionalities and higher molecular weights. Typical of these are polyphenyl polyisocyanate mixtures containing about 20 to 100 wt.% methylene diphenyl diisocyanate isomers, of which 20 to about 95 wt.% thereof is the 4,4'-isomer with the remainder being polymethylene polyphenyl polyisocyanates of higher molecular weight and functionality that have an average functionality of from about 2.1 to about 3.5. The isocyanate mixtures are known, commercially available materials and can be prepared by the process described in U.S. Pat. No. 3,362,979, issued Jan. 9, 1968 to Floyd E. Bentley.

Foaming is carried out in the presence of water and, optionally, additional organic blowing agents. The water is normally used in amounts of 0.5 to 15 parts by weight, preferably, 1.0 to 10 parts by weight (pbw)

based on 100 parts by weight of the polymer polyol and any additional polyol present. The organic blowing agents optionally used along with the water are known in the art and are, for example, monofluorotrichloromethane, difluorodichloromethane, methylene dichloride and others generally known in the art. Additives to regulate the cell size and the cell structure, for example, silicone surfactant such as dimethylpolysiloxanes, may also be added to the foaming mixture. Fillers, flame retarding additives, dyes or plasticizers of known types may also be used. These and other additives are well known to those skilled in the art.

The preparation of a SAN polymer polyol in accordance with the invention will be illustrated by Example 14. The use of this polymer polyol in making molded polyurethane foams will be illustrated with the aid of Example 15. These examples are intended to illustrate the invention, but are not intended to delineate the expected scope of the invention. For example, it is anticipated that the polymer polyols of the present invention would have utility in the production of slab polyurethane foams.

EXAMPLE 14

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The polymer polyol used in the preparation of the molded polyurethane foam was prepared according to the same procedure as the polymer polyols of Examples 1-13, with the following exceptions. The reactor charge was added under a nitrogen atmosphere to a 100 gallon reactor. After heating the reactor charge to reaction temperature, streams #1, #2 and #3 were added over the specified time period. Upon completion of the stream #2 addition, the reaction mixture was held at 115° C. for 0.5 hours. The reaction mixture was vacuum stripped for 4.75 hours at 1-13 mmHg.

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Charges:		
To Reactor:	104 Kg Thanol SF-5507	(SAN wt. ratio: 75/25)
Stream #1:	55.5 Kg Styrene	
Stream #2:	18.5 Kg Acrylonitrile	
Stream #3:	0.93 Kg Vazo 67 initiator	
Stream #3:	8.33 Kg Thanol SF-5507	
Stream #3:	184 Kg Thanol SF-5507	
Reaction Conditions:		
Reaction Temperature:	115° C.	
Stream #1 Addition Time:	120 min.	
Stream #2 Addition Time:	130 min.	
Stream #3 Addition Time:	120 min.	
Polymer Polyol Properties		
Viscosity, cps	2890	
Particle size, μ m	0.67	
Centrifugable solids, wt. %	2.5	

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EXAMPLE 15

This example will show the use of the polymer polyol of Example 14 in the preparation of a molded polyurethane foam.

A polyurethane foam was prepared by charging the amounts of polyol, water, catalysts, and surfactant indicated into a one-liter, cylindrical container equipped with a mechanical stirrer. The mixture was stirred for about 30 seconds at 5,000 to 6,000 rpm and the indicated amount of isocyanate was introduced into the container with stirring for about 5 seconds. The contents of the container were then immediately poured into an aluminum mold preheated to 150° F and was cured in the mold 5 minutes at 200° F. The foam was then demolded, crushed, and allowed to stand at room temperature for about one week. This Example demonstrates that polyurethane foams with good load bearing properties may be made with the polymer polyols of the present invention.

FORMULATION		parts by wt.
Thanol SF-5505		40
Polymer Polyol of Ex. 14		60
Water		3.5
Diethanolamine		1.0
DC 5043 ¹		1.0
Niax A1 ²		0.15
Dabco 33LV ³		0.50
T-12 ⁴		0.01
TDI Index		102
Foam Physical Properties		
ILD, newtons	25%	29.2
	50%	55.6
	65%	87.1
Density, pcf		1.91
Compression set	50%	18.8
	75%	16.9
Tear, pli		1.90
Tensile, psi		23
Elongation, %		110

¹ Silicon surfactant, made by Union Carbide Corp.

² Amine catalyst, made by Union Carbide Corp.

³ Amine catalyst, made by Air Products and Chemicals, Inc.

⁴ Tin catalyst, made by Air Products and Chemicals, Inc.

GLOSSARY

Modified ARCOL® 1372

A glycerin initiated polyether of propylene oxide and ethylene oxide modified with the diglycidyl ether of bisphenol A, with a hydroxyl number of 25 and a primary hydroxyl group content of 80% of the total hydroxyl content of the polyether, made by ARCO Chemical Co.

THANOL® F-3550

A glycerin initiated polyether of propylene oxide and ethylene oxide modified with the diglycidyl ether of bisphenol A, with a hydroxyl number of 48 and containing essentially secondary hydroxyl groups, made by ARCO Chemical Company.

THANOL SF-5505

A glycerin initiated polyether of propylene oxide and ethylene oxide containing about 20% ethylene oxide with a hydroxyl number of 34 and a primary hydroxyl group content of 80% based on the total hydroxyl content of the polyether, made by ARCO Chemical Company.

THANOL SF-5507

A glycerin initiated polyether of propylene oxide and ethylene oxide modified with the diglycidyl ether of bisphenol A, with a hydroxyl number of 34 and a primary hydroxyl group content of 80% based on total hydroxyl content of the polyether, made by ARCO Chemical Company.

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Vazo 67

2, 2'-Azobis(2-methylbutanenitrile) polymerization catalyst made by E.I. duPont de Nemours and Co.

Thus, it is apparent that the use of epoxy resin-modified polyols as base polyols in the preparation of
10 polymer polyols results in the ability to use higher SAN weight ratios, even up to 100/0, and higher polymer solids contents along with acceptable viscosities.

Many modifications may be made in the polymer polyols of this invention and their method of production without departing from the spirit and scope of the invention, which is defined only in the appended claims. For example, one skilled in the art could adjust the temperature, pressure, reactants,
15 proportions and modes of additions within the parameters set forth to provide polymer polyols with particularly advantageous properties, or polymer polyols that give foams with optimal properties.

Claims

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1. A process for making stable, low viscosity polymer polyols comprising polymerising in a reactor, via a free-radical reaction, a monomer component having a styrene portion and an acrylonitrile portion, in the presence of an epoxy resin-modified polyol as the base polyol, where the wt. ratio of the styrene portion to the acrylonitrile portion ranges from greater than 60/40 to 100/0.

25 2. A process as claimed in claim 1 where the monomer component is a mixture of styrene and acrylonitrile in a ratio greater than 60/40.

3. A method for making stable, low viscosity polymer polyols comprising the steps of:-

adding a charge to a reactor, where the charge comprises a first portion of an epoxy resin-modified base polyol;

30 providing a feed stream to the reactor, where the feed stream comprises a second portion of the epoxy resin-modified base polyol, a monomer portion and an initiator suitable for polymerising the monomer portion, where the first portion of the epoxy resin-modified base polyol is less than the second portion.

4. The method as claimed in claim 3 wherein the monomer portion is a mixture of styrene and
35 acrylonitrile in a ratio of styrene to acrylonitrile of from more than 40/60 to 100/0.

5. A method as claimed in claim 3 or 4 where the ratio of the first portion of the epoxy resin-modified base polyol to the second portion thereof is in the range of about 5/95 to about 30/70.

6. A method as claimed in any one of claims 1 to 5 where the epoxy resin-modified base polyol is made by reacting a polyol initiator having an active hydrogen functionality of 3 to 8 and one or more
40 alkylene oxides with an epoxy resin.

7. A method as claimed in claim 6 wherein the epoxy resin is added internally along the length of the resultant epoxy resin-modified polyol.

8. A method as claimed in any one of claims 1 to 7 where the epoxy resin-modified base polyol is made by adding from about 0.25 to about 5.0 wt % epoxy resin, based on the final base polyol.

45 9. A method as claimed in any one of claims 1 to 7 where the epoxy resin-modified base polyol is made by adding from about 0.25 to about 2.0 wt % epoxy resin, based on the final base polyol.

10. A method as claimed in any one of claims 1 to 7 where the epoxy resin-modified base polyol is made by adding from about 0.5 to about 1.5 wt % epoxy resin, based on the final base polyol.

11. A method as claimed in any one of claims 1 to 10 where the polymer polyols are made in the
50 absence of an added dispersant.

12. A method as claimed in any one of claims 1 to 11 where the reactor is selected from the group of reactors consisting of a batch reactor, a semi-batch reactor and at least one continuous stirred tank reactor (CSTR).

13. Stable, low viscosity polymer polyols obtained by the process claimed in any one of claims 1 to 12.

55 14. Stable, low viscosity polymer polyols as claimed in claim 13 having a viscosity of approximately 8,000 cps or less.

15. Stable, low viscosity polymer polyols as claimed in claim 13 or claim 14 having a particle size of about 5.0 μm or less.

16. A polyurethane product made by a process comprising reacting a polymer polyol as claimed in any one of claims 13 to 15 with an organic polyisocyanate in the presence of a polyurethane catalyst.

5 Claims for the following Contracting State:ES

1. A process for making stable, low viscosity polymer polyols comprising polymerising in a reactor, via a free-radical reaction, a monomer component having a styrene portion and an acrylonitrile portion, in the presence of an epoxy resin-modified polyol as the base polyol, where the wt. ratio of the styrene portion to
10 the acrylonitrile portion ranges from greater than 60/40 to 100/0.

2. A process as claimed in claim 1 where the monomer component is a mixture of styrene and acrylonitrile in a ratio greater than 60/40.

3. A method for making stable, low viscosity polymer polyols comprising the steps of:-
adding a charge to a reactor, where the charge comprises a first portion of an epoxy resin-modified base
15 polyol;
providing a feed stream to the reactor, where the feed stream comprises a second portion of the epoxy resin-modified base polyol, a monomer portion and an initiator suitable for polymerising the monomer portion,
where the first portion of the epoxy resin-modified base polyol is less than the second portion.

20 4. The method as claimed in claim 3 wherein the monomer portion is a mixture of styrene and acrylonitrile in a ratio of styrene to acrylonitrile of from more than 40/60 to 100/0.

5. A method as claimed in claim 3 or 4 where the ratio of the first portion of the epoxy resin-modified base polyol to the second portion thereof is in the range of about 5/95 to about 30/70.

6. A method as claimed in any one of claims 1 to 5 where the epoxy resin-modified base polyol is
25 made by reacting a polyol initiator having an active hydrogen functionality of 3 to 8 and one or more alkylene oxides with an epoxy resin.

7. A method as claimed in claim 6 wherein the epoxy resin is added internally along the length of the resultant epoxy resin-modified polyol.

8. A method as claimed in any one of claims 1 to 7 where the epoxy resin-modified base polyol is
30 made by adding from about 0.25 to about 5.0 wt % epoxy resin, based on the final base polyol.

9. A method as claimed in any one of claims 1 to 7 where the epoxy resin-modified base polyol is made by adding from about 0.25 to about 2.0 wt % epoxy resin, based on the final base polyol.

10. A method as claimed in any one of claims 1 to 7 where the epoxy resin-modified base polyol is made by adding from about 0.5 to about 1.5 wt % epoxy resin, based on the final base polyol.

35 11. A method as claimed in any one of claims 1 to 10 where the polymer polyols are made in the absence of an added dispersant.

12. A method as claimed in any one of claims 1 to 11 where the reactor is selected from the group of reactors consisting of a batch reactor, a semi-batch reactor and at least one continuous stirred tank reactor (CSTR).

40 13. A method as claimed in any one of claims 1 to 12 wherein the monomer component is polymerised in the presence of the epoxy resin-modified polyol to give polymer polyols having a viscosity of approximately 8,000 cps or less.

14. A method as claimed in any one of the preceding claims which is operated to obtain polymer polyols having a particle size of about 5.0 μm or less.

45 15. A method of obtaining a polyurethane, said method comprising reacting an organic polyisocyanate in the presence of a polyurethane catalyst with a polymer polyol obtained by the process claimed in any one of the preceding claims.

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(12)

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(54) **High styrene content stable polymer polyols using epoxy resin-modified polyols as base polyols.**

(57) Low viscosity polymer polyols having styrene/acrylonitrile ratios, which may be as high as 95/5 or even 100/0, and good stability are obtained by polymerising a monomer component having a styrene portion and an acrylonitrile portion in the presence of an epoxy resin-modified polyol as the base polyol. The epoxy resin-modified polyols useful as base polyols are preferably made by reacting a polyol initiator having an active hydrogen functionality of 3 to 8 and one or more alkylene oxides with an epoxy resin. Preferably, only a small part of the epoxy resin-modified base polyol is initially charged to the reactor, and the balance forms a part of the monomer feed stream to the reactor.

EP 0 343 907 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 30 5173

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A	EP-A-0 177 192 (ARCO) * Page 6, line 33 - page 9, line 1; examples 1-6; claims 1-9 * & US-A-4 539 339 (Cat. D) ---	1-16	C 08 G 18/63 C 08 G 18/64
A	EP-A-0 231 000 (UNION CARBIDE CORP.) * Page 2, line 23 - page 3, line 3; page 8, line 9 - page 13, line 5; example 2; claim 1 * ---	1-6	
A	EP-A-0 130 405 (UNION CARBIDE CORP.) * Page 8, line 17 - page 20, line 9; claims 1-10 * & US-A-4 495 341 (Cat. D) -----	1-16	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 08 G
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 15-02-1990	Examiner BOURGONJE A. F.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ----- & : member of the same patent family, corresponding document	